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SMELTING OF DURHAM RESOURCES STIBNITE CONCENTRATE TO PRODUCE METALLIC ANTIMONY

by

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SMELTING OF

DURHAM RESOURCES STIBNITE CONCENTRATE

TO PRODUCE METALLIC ANTIMONY

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SMELTING OF DURHAM RESOURCES STIBNITE CONCENTRATE TO PRODUCE METALLIC ANTIMONY

by

J.M. Skeaff

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SMELTING OF DURHAM RESOURCES STIBNITE CONCENTRATE TO PRODUCE METALLIC ANTIMONY

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ABSTRACT

Testwork on the smelting of the Durham Resources stibnite concentrate has been conducted with the objective of determining the best conditions of producing metallic antimony. Both charcoal and iron were used as the reductants. The best recovery of antimony with charcoal as the reductant was only ~57%, while the recovery with iron as the reductant was ~84%. Possibilities for improving the antimony recovery are discussed.

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INTRODUCTION

This work was undertaken in response to a request made by Durham Resources Inc. of Prince William, New Brunswick, concerning the smelting of their stibnite concentrates in facilities at CANMET to produce metallic antimony.

Durham Resources produces approximately 500 T/day of a uniquely high grade stibnite concentrate which contains ~65% antimony (1). (Pure Sb_2S_3 contains 71.72% antimony.) Its traditional client for the concentrate in the U.S. has been obliged to cease operations because of environmental regulations and Durham is presently shipping its concentrate to a European purchaser.

Durham is therefore now giving serious consideration to producing primary antimony metal and crude antimony oxide (Sb_2O_3) which may have higher market prices than the concentrate. Such a development would be of significant benefit to the company and the region and would be consistent with EMR policy of encouraging further processing in Canada.

The methods of producing antimony or its oxide are treated in detail elsewhere (2,3). Generally, low or medium grade ores or concentrates are initially treated by liquation, in which the material is subjected to controlled heating to melt the Sb_2S_3 which runs into receptacles, or by roasting in air in which the material is converted to the volatile Sb_2O_3 which is then recovered in baghouses and ESP's. However, these methods are essentially concentration processes which should not be required for high grade concentrates such as Durham's.

The production of the metal from high grade stibnite ores or concentrates may be accomplished by the English precipitation method (2) which consists of the reduction of the stibnite with iron under a flux of soda ash [Na_2CO_3]:

$$Sb_2S_3 + 3\ Fe = 3\ FeS + 2\ Sb. \qquad [1]$$

It may also be accomplished by using carbon or charcoal as a reductant:

$$Sb_2S_3 + 3\ Na_2CO_3 + 6C = 2\ Sb + 3\ Na_2S + 9\ CO, \qquad [2]$$

although antimony losses of 30-40% in the form of such complexes as sodium thioantimonate [Na_3SbS_4]) to the sodium carbonate slag occur (2) which apparently may be recovered only by uneconomic methods. The reduction is conducted in a reverberatory furnace at ~1000°C and appears to be accompanied by the evolution of a significant amount of Sb_2O_3 fume (5-40% of the concentrate (3)) which must be recovered in baghouses for secondary treatment.

Additionally, both carbon and iron may be simultaneously used as reductants as the precipitation method in a reverberatory furnace (2). The antimony produced by these methods requires re-

fining.

The specifications set by the Japanese Standards Association (JSA) for antimony are as follows:

	Sb	Pb	As	Fe	S	Cu	Ni	Bi	Sn
Special Class	≥99.50	0.20	0.10	0.05	0.10	0.05	0.05	0.01	0.05
Class 1	≥99.00	0.60	0.20	0.10	0.20	0.10	0.10	0.04	0.10
Class 2	≥98.50	-	-	-	-	-	-	-	-

The ASTM no longer has a specification for antimony.

The objective of the testwork conducted at CANMET was to determine the optimum temperatures, retention times, reductants and fluxes which will produce a primary antimony suitable for oxidation to Sb_2O_3 or refining if required.

The work was conducted in two stages, the first on a small static scale to determine the optimum flux composition, reductant and antimony recovery with a view to maintaining as low a temperature as possible to minimize losses of antimony due to volatilization. Upon determination of the best conditions for smelting of the concentrate, the second stage was conducted on a 2 kg scale in a 30 kW induction furnace.

EXPERIMENTAL

Materials

Stage 1

Given in Table 1 are the analyses of the concentrate as supplied by Durham Resources and the compositions in percentages, %, and mole fractions, n, of the fluxes used for each of the tests in this stage. One hundred grams of concentrate were used for each test.

The compositions of the fluxes were calculated from the compilations in "Phase Diagrams for Ceramists" (4) to give minimum melting temperatures.

The fluxes used were reagent grade chemicals obtained from suppliers such as Fisher and Anachemia.

Stage 2

The fluxes used were bulk grade chemicals obtained from suppliers such as Fisher and Anachemia.

TABLE 1: Compositions of Concentrate and Fluxes used in Static Crucible Tests

material	wt,kg	Sb wt %	Fe wt %	As wt %	C wt %
concentrate supplied by Durham	20.91	64.6	1.31	0.17	-
coke supplied by CANMET	-	-	-	-	91.5

	test no.															
	1		2		3		4		5		6		7		8	
Flux	wt,g	n	wt,g	n	wt,g	n	wt,g	n	wt,g	n	wt,g	n	wt,g	n	wt,g	n
Na2CO3	86.4	0.80	69.2	0.64	69.2	0.64	77.8	0.72	69.2	0.64	86.4	0.80	86.4	0.80	86.4	0.80
NaCl			23.4	0.32	23.4	0.32	21.0	0.36	23.4	0.32			23.4	0.16		
CaF2			12.5	0.16											12.48	0.16
CaCO3					16.0	0.16									4.00	0.04
CaO			2.24	0.04	2.24	0.04	5.60	0.10	1.68	0.03	1.68	0.03				
CaCl2									18.84	0.17	18.84	0.17				

Procedure

Stage 1

1. The test series were conducted with iron powder and with charcoal as the reducing agents in proportions calculated from reactions 1 and 2 plus a 5% excess. Preliminary testwork indicated that the most suitable temperatures for iron as the reductant were 750° and 800°C and for charcoal as the reductant were 800° and 850°C.

2. The components of the charges were weighed and mixed in a rotary blender for ~0.5 hr prior to charging to the furnace, which was a Lindberg 51000 series box furnace equipped with a stainless steel controlled atmosphere retort capable of operation to 1200°C.

3. For the charcoal reductant series, the tests were conducted in a flowing inert atmosphere of argon to prevent the oxidation of the charcoal prior to reaction with the stibnite. For the iron reductant series, the tests were conducted in a flowing atmosphere of air, since there was little indication of iron oxidation prior to reaction with the stibnite.

4. Upon completion of the 1 hr retention time, the furnace was cooled to room temperature and the crucibles were removed and weighed. The metal buttons were separated from the slags, weighed at Durham Resources, Prince William, N.B., and analysed at K-F Laboratories, Fredericton, for Sb, As and Fe. The weights of both slag and metal as determined by Durham Resources (1) are given in the Appendix.

Stage 2

In this stage, the reduction smelting tests were conducted in a 30 kW Inductotherm induction furnace. The charges were fed to Noltina Carbond (carbon bonded silicon carbide) no. 16 crucibles (capacity 3.5 L) obtained from Stackpole Industries, Toronto. The crucible was covered with a three-holed Fibrefax plate of 1" thickness fitted with a 1.5" i.d. Vitrosil venting stack and a 1.25" i.d. Alundum feeding tube.

Charges of stibnite concentrate, coke and sodium carbonate or of stibnite concentrate and iron were mixed in the stoichiometric proportions indicated by reactions 1 and 2, plus a 5-10% excess.

Approximately 300 g of the mixed flux were added to the crucible and heating was commenced. After the flux had melted at approximately 800°C, the temperature was increased to approximately 1000°C and the charge was introduced into the furnace through the feed tube with a scoop in approximately 100 g quantities at a time.

TABLE 2: Antimony Recoveries with Iron as Reducant

flux	SAMPLE DESCRIPTION		ANTIMONY(%)	ARSENIC(%)	IRON(%)	antimony recovery, %
Na_2CO_3	A 750 Fe - 1	METAL	64.5	0.26	3.43	51.7
" + NaCl + CaF_2 + CaO	2		64.7	0.19	3.48	61.6
" + NaCl + $CaCO_3$ + CaO	3		87.7	0.21	4.99	86.1
" + CaO	4		85.2	0.21	4.32	83.1
" + NaCl + CaO + $CaCl_2$	5		74.2	0.16	5.02	67.7
" + CaO + $CaCl_2$	6		88.3	0.30	3.90	84.5
" + NaCl	7		87.2	0.23	5.97	88.4
" + CaF_2 + $CaCO_3$	8		89.7	0.21	4.62	86.1
	A 750 Fe - 1	SLAG	11.4			
	2		3.05			
	3		2.99			
	4		3.44			
	5		3.98			
	6		3.83			
	7		1.98			
	8		4.50			

flux	SAMPLE DESCRIPTION		ANTIMONY(%)	ARSENIC(%)	IRON(%)	antimony recovery, %
Na_2CO_3	A 800 Fe - 1	METAL	92.5	0.20	3.62	67.6
" + NaCl + CaF_2 + CaO	2		93.2	0.22	4.68	91.6
" + NaCl + $CaCO_3$ + CaO	3		93.5	0.23	5.76	92.5
" + CaO	4		95.1	0.19	4.26	93.8
" + NaCl + CaO + $CaCl_2$	5		96.2	0.17	2.36	92.3
" + CaO + $CaCl_2$	6		96.2	0.17	3.36	94.0
" + NaCl	7		97.1	0.14	2.00	96.9
" + CaF_2 + $CaCO_3$	8		95.4	0.19	4.22	91.6
	A 800 Fe - 1	SLAG	12.9			
	2		2.53			
	3		2.38			
	4		2.24			
	5		2.92			
	6		2.47			
	7		2.36			
	8		3.20			

TABLE 3: Antimony Recoveries with Charcoal as Reducant

flux	SAMPLE DESCRIPTION		ANTIMONY(%)	ARSENIC(%)	IRON(%)	antimony recovery, %
Na_2CO_3	B 800 C - 1	METAL	73.4	0.15	0.27	24.7
" + NaCl + CaF_2 + CaO	2		98.5	0.20	0.07	42.7
" + NaCl + $CaCO_3$ + CaO	3		99.4	0.12	0.08	24.9
" + CaO	4		98.5	0.15	0.14	30.5
" + NaCl + CaO + $CaCl_2$	5		99.5	0.12	0.08	28.0
" + CaO + $CaCl_2$	6		98.2	0.14	0.08	33.4
" + NaCl	7		96.9	0.17	0.08	32.7
" + CaF_2 + $CaCO_3$	8		97.5	0.17	0.08	40.8
	B 800 C - 1	SLAG	17.6			
	2		12.8			
	3		16.8			
	4		16.3			
	5		13.7			
	6		15.7			
	7		15.3			
	8		14.2			

flux	SAMPLE DESCRIPTION		ANTIMONY(%)	ARSENIC(%)	IRON(%)	antimony recovery, %
Na_2CO_3	B 850 C - 1	METAL	99.0	0.20	0.04	54.3
" + NaCl + CaF_2 + CaO	2		99.1	0.23	0.04	56.0
" + NaCl + $CaCO_3$ + CaO	3		98.2	0.20	0.05	48.6
" + CaO	4		96.0	0.21	0.03	53.2
" + NaCl + CaO + $CaCl_2$	5		98.2	0.20	0.05	43.9
" + CaO + $CaCl_2$	6		97.8	0.19	0.04	55.7
" + NaCl	7		98.5	0.22	0.03	53.1
" + CaF_2 + $CaCO_3$	8		98.5	0.21	0.03	54.7
	B 850 C - 1	SLAG	12.2			
	2		10.7			
	3		13.0			
	4		10.8			
	5		13.0			
	6		10.0			
	7		10.4			
	8		11.6			
	CRUCIBLE, CARBON RUNS		0.80			

Upon completion of the addition of the charge, the molten mass was allowed to stand at temperature for the indicated time period, after which the furnace power was turned off and the charge was allowed to cool in place. When the charge had cooled to room temperature, the slag and metal were separated as completely as possible and the metal was weighed; samples of both were analysed by K-L Laboratories for Sb, As, Pb and, for the test in which iron was used as reductant, Fe.

The antimony recoveries for both stages were calculated from:

$$\text{Sb recovery \%} = (W_{metal} \times A_{Sb}) / (W_{conc} \times 0.646) \qquad [4]$$

in which

W_{metal} = the weight of the metal recovered;

A_{Sb} = the assay of antimony in the recovered metal; and

W_{conc} = the weight of stibnite concentrate used in the test.

RESULTS AND DISCUSSION

Stage 1

The antimony recoveries from the small scale crucible tests with iron and with charcoal as reductants are given in Tables 2 and 3 respectively. Average weight losses are given in Table 4.

TABLE 4: Average Percentage Weight Losses in Small Scale Crucible Tests

	temperature, °C		
reductant	750	800	850
iron	6.5	6.9	-
charcoal	-	12.3	15.3

Iron as the reductant

The data of Table 2 indicate that a temperature of at least 800°C is required to obtain antimony recoveries in excess of 90% with iron as the reducing agent. At 750°C, the antimony recoveries do not exceed ~88%.

It will be noted that with only Na2CO3 as the flux, reco-

veries of antimony are only ~52% and 68% at 750° and 800°C respectively. This is not unexpected since Na_2CO_3 is not liquid until 856°C and hence the reduction would be essentially a solid-solid reaction. Since the percentage weight losses with iron as the reductant are not large, slag losses would account for most of the remainder of the unrecovered antimony.

With the other fluxes, the recoveries of antimony are significantly higher, and attain a maximum of 96.9% with Na_2CO_3 + NaCl (flux no. 7) at 800°C. This flux also produced the purest antimony, analysing 97.1% Sb, 0.14% As and 2.00% Fe. It is interesting to note that the arsenic contents in the antimony buttons produced with iron as the reductant at 800°C generally meet the specifications of the JSA for Class 1 metal, although the lowest iron level, 2%, is too high for the specification. Therefore flux composition no. 7 was chosen for the induction furnace test in which iron was the reductant.

Charcoal as the reductant

The data of Table 3 indicate that a temperature of at least 850°C is required to obtain antimony recoveries in excess of 50% with charcoal as the reducing agent. At 800°C, the antimony recoveries are very poor and do not exceed ~43%.

It will be noted that with pure Na_2CO_3 as the flux, the recovery of antimony is only ~25% at 800°C; at 850°C the recovery increases to ~54%. This is not unexpected since, as noted above, Na_2CO_3 is not liquid until 856°C and hence the reduction would be essentially a solid-solid reaction. Since the stoichoimetric weight loss (exclusive of volatilization losses) for reaction 2 going to completion is 34.54%, it is evident from the weight losses in Table 4 that the reaction between the stibnite concentrate and the Na_2CO_3 plus carbon was quite incomplete. Additionally, as seen from the data in Table 3, losses of antimony to the slag are in the order of 10-13% at 850°C.

With the other fluxes, the recoveries of antimony are not significantly higher, although a maximum of 56% was attained with Na_2CO_3 + NaCl + CaF_2 + CaO (flux no. 2) at 850°C. This flux also produced the purest antimony, analysing 99.1% Sb, 0.23% As and 0.04% Fe. It is interesting to note that this antimony metal meets the specifications of the JSA for Class 1 metal for Sb, As and Fe. Therefore flux composition no. 2 was chosen for the induction furnace test in which coke was the reductant.

Stage 2

The results of the induction furnace tests are presented in Table 5. Preliminary reduction tests with the induction furnace indicated that a minimum temperature of 1000°C was required to maintain a slag of sufficient fluidity to allow additions to be made to the melt and to allow the reduction to proceed. The power requirement to maintain this temperature was 14-16 kW.

TABLE 5: Product Recoveries and Analyses from Induction Furnace Smelting Tests

Feed for all tests consisted of 1500 g of stibnite concentrate (containing 969 g Sb and 382 g S) plus the indicated amounts of flux and reductant

test no.	feed				products										
			net wt. loss				Sb			S			As	Pb	Fe
	material	wt,g	g	%	material(1)	wt,g	wt %	wt,g	dist %	wt %	wt,g	dist %	wt %	wt %	wt %
310786	Na2CO3	1392	1502	41.7	metal	571	96.5	551	56.86	-	-	-	0.22	0.43	-
	coke	375			matte		8.9			12.5	-	-	-	-	-
	flux #2	332			slag	1526	8.8	134	13.86	9.3	142	37.15	0.01	0.01	-
								685	70.72		142	37.15			
050886	Na2CO3	1392	1626	44.4	metal	562	96.6	543	56.03	-	-	-	0.20	0.38	-
	coke	375			matte		4.5			11.0	-	-	-	-	-
	flux #2	395			slag	1475	9,9	146	15.07	10.0	148	38.74	0.01	0.02	-
								689	71.10		148	38.74			
070886	Na2CO3	1392	1724	43.0	metal	581	94.4	548	56.60	-	-	-	0.19	0.41	-
	coke	375			matte		4.5			8.1	-	-	-	-	-
	flux #2	395			slag	1704	10.2	174	17.94	6.7	114	29.89	0.01	0.02	-
	iron	250													
								722	74.54		114	29.89			
080886	iron	700	515	18.3	metal	860	85.4	734	75.79	-	-	-	0.18	0.41	14.4
	flux #7	615			metal(fines)	99	77.9	77	7.96	-	-	-	0.20	0.18	16.4
					slag	1440	3.2	46	4.76	16.0	230	60.31	-	-	-
								857	88.51		230	60.31			

(1) Weight of slag includes weight of matte

Three of the four induction furnace tests reported here were conducted with coke as the reductant, since Durham Resources were more interested in using this as a reductant rather than iron.

310786

In this test, the temperature was maintained as close to 1000°C as possible. Upon the addition of concentrate, coke and sodium carbonate flux in ~100 g quantities to the crucible, the white fume of antimony oxide would usually be exhausted from the venting stack, although the fume would sometimes be black or brown as an indication of unreacted charge release. During the one-half hour needed to make the material additions, the melt was quite fluid and agitated. Following completion of the additions, the melt gradually became more viscous, to the point when at the end of the one hour hold time, the melt was essentially a solid-liquid slurry exhibiting little movement.

The net weight loss for this test was 1502 g or 41.7% of the net total charge. As previously noted, the stoichiometric weight loss calculated from completed reaction 2 is 34.54% of the un-fluxed charge or 1128 g due to the formation and release of carbon monoxide gas. However, on the basis of nine moles of CO released for each two moles of antimony produced in this test as in reaction 2, the weight loss should be 570 g or 15.8% of the net total charge. Additional weight losses can be calculated to be 395 g of Sb_2S_3 on the basis of the 70.72% accountability of antimony and the assumption that the unaccounted for antimony was volatilized as the oxide formed by

$$Sb_2S_3 + 9/2\ O_2 = Sb_2O_3 + 3\ SO_2. \qquad [5]$$

Hence the formation of CO and the losses of antimony through the oxidation of the sulphide account for 965 g or ~64% of the actual losses. Further losses could occur from the evolution of CO_2 from the Na_2CO_3 flux and coke entrained with the Sb_2O_3. Finally, losses could occur due to the volatilization of Sb_2S_3 because its vapour pressure at 1000oC is close to one atmosphere (5), which would account for the brown fume evolved during charging as noted above.

When the crucible was broken open, it was evident that three phases had been formed during the reduction. These consisted of a well-formed metal skull at the bottom of the crucible, on top of which had formed a solid, reddish-brown phase designated as a matte, and on top of this, a black, porous slag phase interspersed with metallic prills. The matte phase was readily separated from the metal button. However, because the matte and slag phases were difficult to separate from each other, only a sample of the former was taken for analysis, and hence the slag weight given in Table 5 was determined by weight differences and includes the weight of the matte phase.

It is seen from Table 5 that the total extraction of antimony metal (as represented by the distribution % of metal for the

test) is only ~57%. This level of antimony recovery is close to the lower end of the range (60-70%) of that indicated by Wang (2) for the use of charcoal as a reductant, although he notes that slag losses account for most of the unrecovered antimony whereas the antimony accountability of ~71% reported here would indicate that a significant amount of the antimony was lost as unreacted fines or as the volatile oxide or sulphide during the addition of material to the crucible. These losses may be due to the configuration of the feeding system and may be reduced by improved smelting procedures.

It will be noted from the data of Table 5 that the sulphur contents of the matte and slag were 12.5 and 9.3% respectively. However, on the basis of three moles of Na_2S formed for each two moles of antimony produced in this test as in reaction 2, the total amount of sulphur in both phases should be 217 g, which is considerably more than the 142 g calculated for the slag plus matte. More extensive analyses, the separation of matte and slag and the recovery of the exhausted dust and fume would be required to enable a complete mass balance.

050886

In this test, the temperature was maintained as close to 1100°C as possible to determine whether the antimony recoveries could be improved by increasing the temperature. Comments similar to the above concerning material addition to the crucible and the amount of agitation with time are also valid for this test.

The net weight loss during the reduction was ~44%, similar to that for 310786. Comments similar to the above concerning weight losses and antimony accountability are also valid for this test.

As above, when the crucible was broken open, it was evident that three phases had been formed during the reduction: the metal skull, the reddish-brown matte and the black, porous slag phase interspersed with metallic prills. The separations of the phases proceeded as above so that the slag weight given in Table 5 includes the weight of the matte phase for this test.

As for test 310786, it is seen from Table 5 that the total extraction of antimony metal is only ~56%, so that there is no significant effect of temperature on the recovery of antimony. Again, the antimony and sulphur accountabilities of ~71% and ~79% respectively would indicate that a significant amount of the antimony was lost as the volatile oxide, sulphide or unreacted fines during the addition of material to the crucible.

070886

In this test, upon completion of the material additions as in the other tests noted above, iron metal filings were added to the melt to determine whether iron could displace some of the antimony from the slag and matte and thereby improve the metal

recoveries. The temperature was maintained as close to 1000°C as possible since 050886 had not shown any antimony recovery dependence on temperature. Comments similar to those made above concerning material addition to the crucible and the amount of agitation with time are also valid for this test. The iron filings appeared to react vigorously with the slag.

The net weight loss during the reduction was 43%, similar to that for 050886. Comments similar to those made for 310886 concerning weight losses and antimony accountability are also valid for this test. The significantly lower sulphur accountability would suggest the formation and oxidation of FeS to form SO_2 and hematite or magnetite.

As in the previous tests, when the crucible was broken open, it was evident that three phases had been formed during the reduction: metal, matte and black, porous slag interspersed with metallic prills. The separation of the metal skull from the matte was not accomplished cleanly and the top of the skull therefore contained many matte inclusions. However, the bulk of the skull was clean. Otherwise, the separations of the phases proceeded as before so that the slag weight given in Table 5 includes the weight of the matte phase for this test.

As with test 050886, it is seen from Table 5 that the total extraction of antimony metal is only ~57%, so that it is evident that the iron additions subsequent to the additions of concentrate, coke and flux did not improve on the recovery of antimony. Again, the antimony and sulphur accountabilities of ~75% and ~30% respectively would indicate that a significant amount of the antimony was lost as the volatile oxide, sulphide or unreacted fines during the addition of material to the crucible. It is also clear from the increased slag weight over that of the previous two tests that most of the iron reported to the slag, although it would appear from the slightly heavier skull and its lower antimony content that a small amount of the iron also reported to the metal skull.

080886

This test was conducted to determine whether iron metal filings as the reductant would improve on the recoveries of antimony over those with coke. The charge addition was initiated at 900°C but the temperature had to be increased to 1000°C to maintain a slag of adequate fluidity. The iron filings appeared to react vigorously with the stibnite concentrate upon contact with the slag. The melt was left to digest for ~30 min.

The net weight loss during this reduction was 515 g or ~18% of the total net weight added, which, although significantly less than for the tests with coke as the reductant, is greater than anticipated since no weight change is indicated by reaction 1. One weight loss can be calculated to be 155 g of Sb_2S_3 on the basis of the 88.51% accountability of Sb and the assumption that the unaccounted for Sb was volatilized as the oxide formed accor-

ding to reaction 5. Other losses could be from the evolution of CO_2 from the Na_2CO_3 flux and fine iron powder entrained with volatilized Sb_2O_3 and Sb_2S_3. As with the coke reductant tests, more extensive analyses and the recovery of the exhausted dust and fume would be required to enable a complete mass balance.

When the crucible was broken open, it was evident that only two phases had been formed during the reduction: metal and a dense greenish-black slag. As with 070884, the separation of the metal skull from the slag was not accomplished cleanly and a zone of metal interspersed with slag had formed between the two bulk phases. Continuous washing was used to recover the metal fines from the slag. However, the bulk of the skull was free of slag. The absence of a separate iron sulphide phase indicates that the FeS would have dissolved in the slag.

In contrast to the other tests reported here, it is seen from Table 5 that the total extraction of antimony metal, including that obtained from the fines, is ~84%, so that it is evident that iron as a reductant is considerably more efficient than coke. The antimony accountability of ~89% reported here would indicate that, although significant, the amount of antimony lost as the volatile oxide, sulphide or unreacted fines during material charging was considerably less than with coke as the reductant. It is also clear from the iron analysis that the metal contained ~15% iron, with the slag presumably containing the remaining 560 g of the charged iron.

On the basis of reaction 1, for each two moles of antimony produced in this test, the slag should contain 320 g of sulphur. That the slag contains only 230 g of sulphur would suggest the possibility of the oxidation of FeS to form SO_2 and hematite or magnetite. As noted above, more complete analyses are required to conduct a mass balance.

The metals produced in all four tests reported above meet the JSA standard for As and Pb, although the antimony contents are clearly less than acceptable.

CONCLUSIONS

From the results reported here, a few conclusions become obvious:

1. With coke as the only reductant and even under optimized conditions, it will be very difficult if not impossible to attain antimony recoveries in excess of the 60-70% indicated by Wang (2), because of the formation of sodium thioantimonate and other thio-complexes of antimony which appear to be lost to the slag.

2. Unless it is found possible to employ iron in a separate cleaning procedure to scavenge antimony from slags produced from carbon reduction, in order to improve on the recovery of antimony, it will be necessary to use iron as the major reductant,

possibly with some coke as suggested by Wang (2) to reduce the amount of iron reporting to the antimony.

3. The metal produced by either of the above methods will contain impurities and will likley require refining by one of the methods discussed by Wang (2).

4. Losses of antimony as the volatile oxide, sulphide or as unreacted concentrate will occur and must be minimized in order to minimize the amount of oxide and sulphide to be recovered in baghouses.

5. Being to some extent water soluble, the slags produced by the smelting of the stibnite concentrate would require environmental control.

Since the tests reported above were only exploratory in nature, it is clear that many changes could be made in the smelting procedures to improve on the quality and recoveries of antimony. Further work could consist of the following:

1. Addition of the complete charge to the crucible at room temperature followed by heating until the reaction is complete as in the Stage 1 tests. This may enable the reaction to proceed at temperatures below 1000°C.

2. Continuous instead of intermittent addition of the charge to prevent surges of reaction and reduce release of Sb_2O_3 and Sb_2S_3.

3. Addition of some of the fluxing agents with the concentrate and reductant to partially prevent the release of antimony as the oxide, sulphide and unreacted concentrate.

4. Agglomeration of the charge into pellets to accomplish the same as 3 above.

5. Optimization of the flux:concentrate ratio to minimize antimony losses to slag.

6. The use of both iron and coke as reductants in optimized proportions. This would cause the formation of both Na2S and FeS which form a range of liquid solutions above ~760°C and therefore may enable the reduction to take place at lower temperatures.

7. Investigation of the following reaction to reduce the consumption of Na_2CO_3 and render sulphur into a less unstable compound than Na_2S:

$$Sb_2S_3 + 3\ CaCO_3 + 6C = 2\ Sb + 3\ CaS + 9\ CO. \qquad [6]$$

8. Investigation of the use of iron to clean antimony from the slags produced with coke as the reductant.

9. Two-thirds scale-down of the charge to provide greater freeboard and reduce gas flowrates within the crucible.

10. The use of a nitrogen purge during material charging to prevent excessive losses of stibnite due to oxidation and volatilization.

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APPENDIX

Weight of Button and Slag

Sample	Button(g)	Slag(g)*
A750 Fe 1	51.8	166.27
2	61.5	177.04
3	63.9	176.76
4	63.0	175.11
5	58.9	184.57
6	61.8	173.57
7	65.5	175.29
8	62.0	169.86

Sample	Button(g)	Slag(g)*
A800 Fe 1	47.2	169.43
2	63.5	175.59
3	63.9	175.34
4	63.7	174.32
5	62.0	179.41
6	63.1	170.90
7	64.5	174.73
8	62.0	167.02

Sample	Button(g)	Slag(g)*
B800 C 1	21.7	291.35
2	28.0	291.68
3	16.2	269.15
4	20.0	262.56
5	18.2	274.50
6	22.0	258.79
7	21.8	266.20
8	27.0	250.72

Sample	Button (g)	Slag(g)*
B850 C 1	35.4	219.00
2	36.5	233.30
3	32.0	244.24
4	35.8	237.16
5	28.9	245.61
6	36.8	232.83
7	34.8	241.87
8	35.9	229.42

* gm Slag = gm In - gm button - gm loss